18. Derive the expressions for thermodynamic functions such as internal energy, entropy. Helmholtz, and Gibbs free energy in terms of the molecular partition function.

19. Derive the phenomenological equations involving force-flux relations.

20. Discuss the kinetics of polymerization reactions with mechanisms.

NOVEMBER/DECEMBER 2025

23PCH22 — PHYSICAL CHEMISTRY – I

Time : Three hours Maximum : 75 marks

SECTION A — (10 × 2 = 20 marks)

Answer ALL questions.

1. What is the limitation of classical thermodynamics?

2. Write the Gibbs-Duhem equation.

3. A system of N particles has, among others, two energy levels with $g_1=2$, $g_2=3$, U1 = 41.84 KJ mol^{-1} and UI =58.58 KJ mol^{-1}. Calculate the ratio of the number of particles in the two energy states at 1000 K.

4. Write an expression for the molecular translation partition function of an ideal gas.

5. State equipartition principle.

6. Give the concept of redisual entropy in thermodynamics.

7. Define thermornechanical effect.

8. Write a biological application of irreversible thermodynamics.

9. State primary salt effect.

10. What do you meant by thermal chain reaction?

SECTION B — (5 × 5 = 25 marks)

Answer ALL questions.

11. (a) Explain the terms fugacity and activity. How are they related to chemical potential?

Or

(b) How activity coefficient determined by EMF method?

12. (a) (i) Calculate the kinetic energy of an ideal gas per molecule and per mole at 27°C.

(ii) Calculate q. w. ΔU and ΔH for the reversible isothermai expansion of one mole of an ideal gas at 27°C from a volume of $10dm^3$ to a volume of 20 dm^3.

Or

(b) Briefly explain Fermi- Dirac statistics.

13. (a) Derive Gibbs-Heluiholmz equation for a process at constant pressure and at constant volume.

Or

(b) Explain Debye model of heat capacity of solids.

14. (a) Write short notes on current flow in open systems.

Or

(b) Discuss electrokinetic effects with examples.

15. (a) Explain the Rice-Herzfeld mechanism for chain reactions.

Or

(b) Discuss the chain reaction maehanism of the H_2- Br_2 reaction.

SECTION C — (3 × 10 = 30 marks)

Answer any THREE questions.

16. Derive and explain the Duhem-Margules equation with its applications.

17. Using the expression for the Maxwell distribution of velocities, draw the distribution at three different temperatures and comment on the shapes of the distribution curves.